Overview of Hydrogen Storage: Gas, Liquid and Solid

Gary Sandrock

Detailee to DOE Headquarters
From Oak Ridge National Laboratories

DOE-EERE/NIST Joint Workshop on Combinatorial Materials Science for Applications in Energy (MCMC-14)
NIST Combinatorial Center
November 5, 2008

Hydrogen Fueled Vehicles

- Fuel Cell and H_2 ICE-Electric Hybrid Vehicles have similar needs.
- Ideally use waste heat of FC or ICE (< 100˚C)
- Demonstration vehicles use mostly high pressure gas storage.

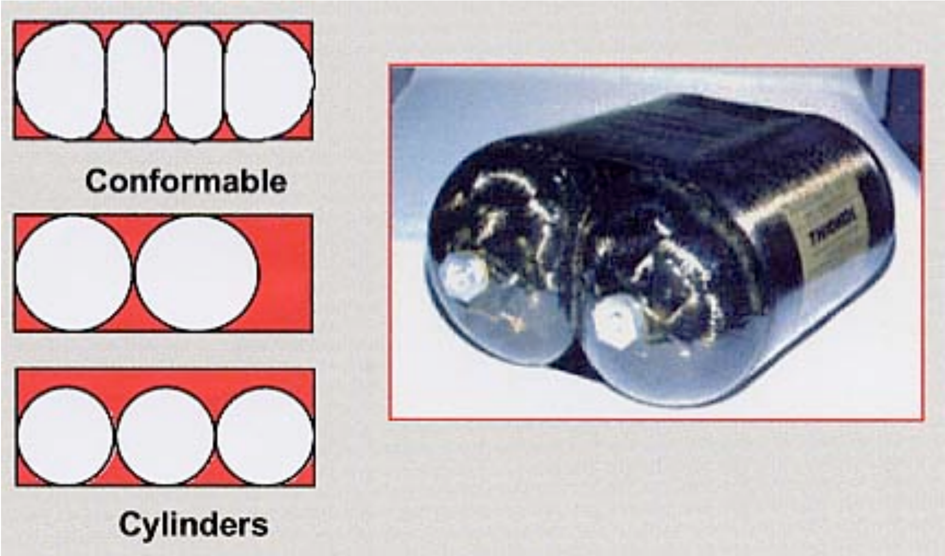
Ford Fuel Cell Car with 700 bar (70MPa) CG Storage - Powertech (BC Hydro of Canada)

Toyota Prius H_2-ICE / Electric Hybrid - ECD Ovonic Hydride Storage

The Three Principal Forms of Hydrogen Storage

Liquid

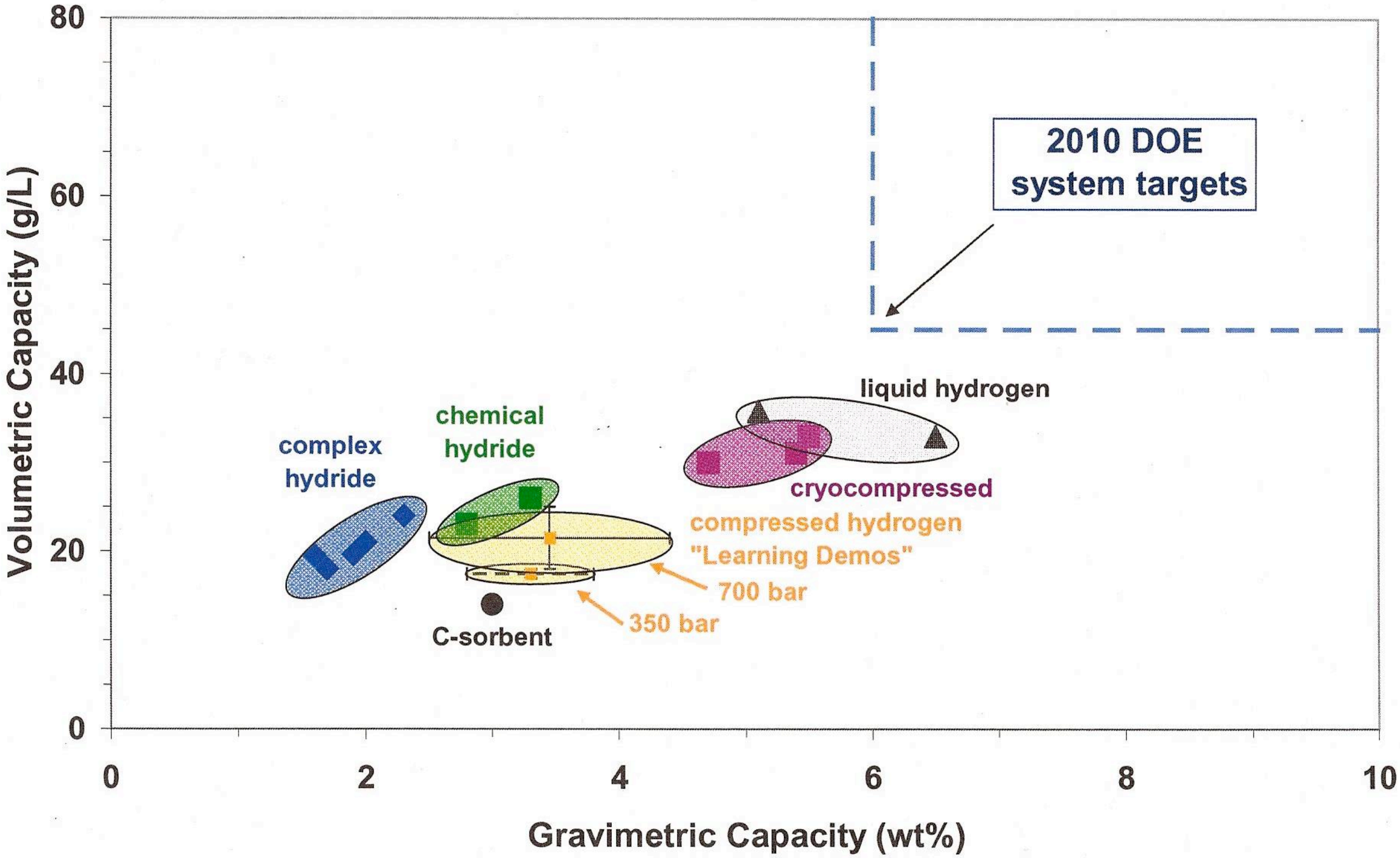
Gas



Solid

Current System Status - 2008

No technology meets targets



SOME HYDROGEN STORAGE METHODS

1. Gaseous hydrogen

A. Steel tanks
B. Composite tanks
C. Cryogas
D. Glass microspheres

2. Liquid hydrogen

A. Cryogenic
B. $NaBH_4$ solutions
C. Rechargeable organic liquids
D. Anhydrous ammonia NH_3

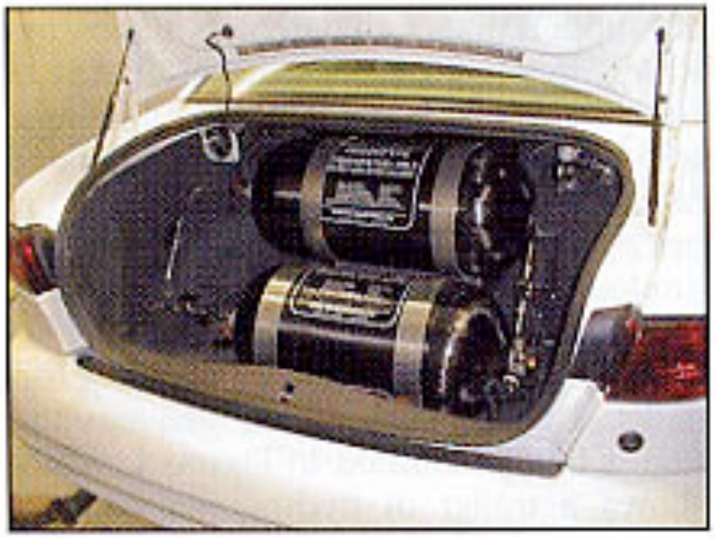
3. Solid hydrogen

A. Chemical hydrides (H_2O-reactive)
- a. Encapsulated NaH
- b. LiH & MgH_2 slurries
- c. CaH_2, $LiAlH_4$, etc

B. Chemical hydrides (thermal)
- a. Ammonia borane
- b. Aluminum hydride
- c. Misc. LE compounds
- d. Nanomaterials (e.g., Si)

C. Carbon & other HSA materials
- a. Activated charcoals
- b. Nanotubes
- c. Graphite nanofibers
- d. MOFs, Zeolites, etc.
- e. Clathrate hydrates
- f. Polymeric adsorbers

D. Rechargeable metal hydrides
- a. Alloys & intermetallics
- b. Nanocrystalline
- c. Complex



High-pressure H_2-storage in C-fiber-wrapped composite tanks

P = 35-70 MPa (350-700 bar)

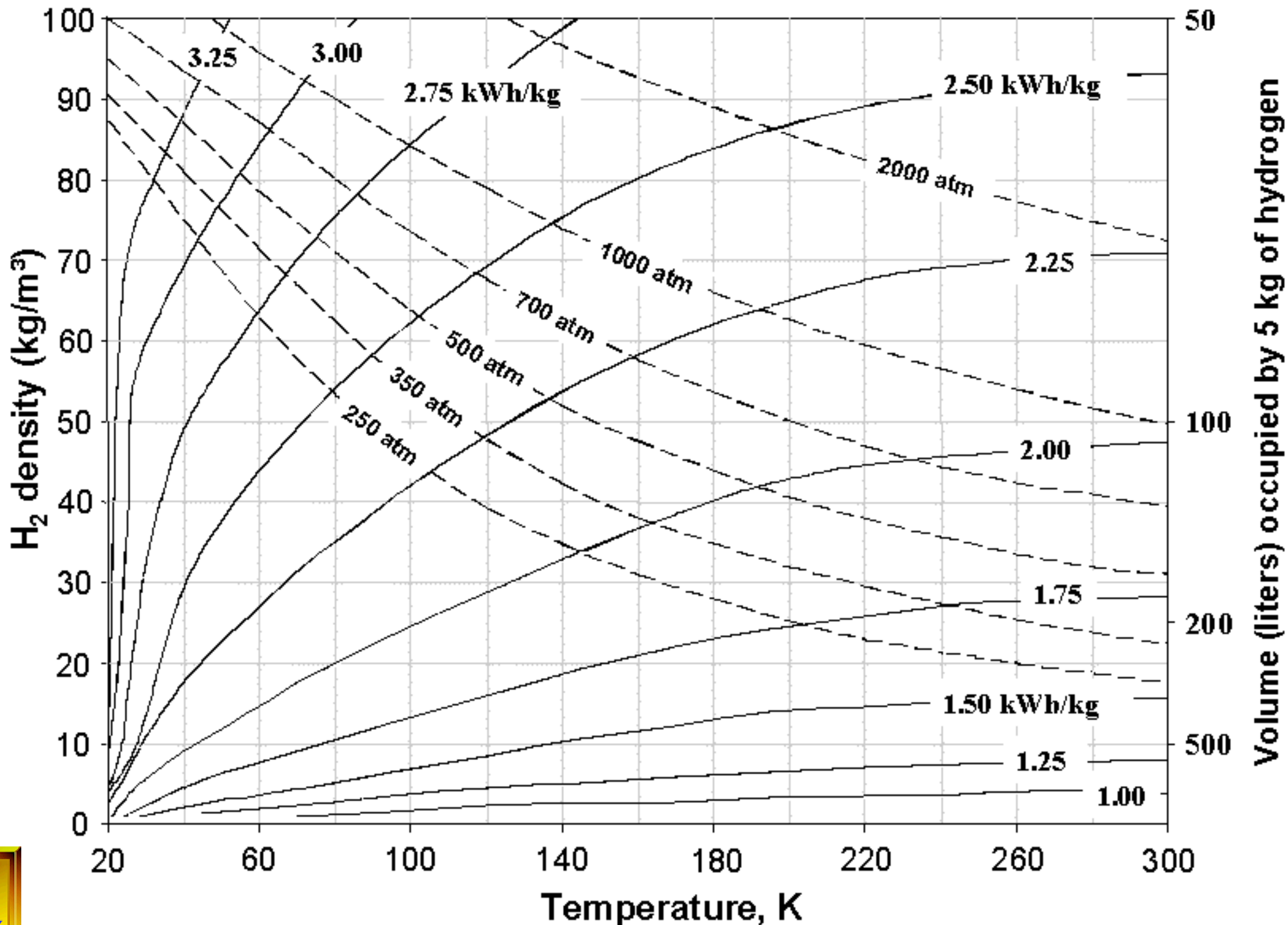
Advantages:

1. Moderately low weight
2. Commercially available
3. Well engineered and safety tested
4. Code accepted in several countries to 350-700 bar
5. No internal heat exchange
6. Much prototype experience
7. May be usable for cryogas

Disadvantages:

1. High volume (cannot meet target)
2. Expensive ($500-600/kg H)
3. Very high pressures mean high compression energy penalties
4. Rapid loss of H_2 in accident
5. Long-term materials uncertainties under cyclic or cold conditions
6. Ideal (cylindrical) shape difficult to conform to available space

Cryocompressed H_2 for Increased Density



Aceves, Berry et al, LLNL, 2007

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Cryogenic Liquid Hydrogen - LH_2

Basic properties of LH_2:

Normal Boiling Point = 20.3K = -253˚C

Density at NBP = 70.8 kg/m^3

Critical Pressure = 1.3 MPa (12.8 atm)

Critical Temperature = 33.0K

H-Capacities:

H_2 Density	Theoretical	System
Gravimetric, wt.%	100	5-7
Volumetric, kg/m^3	70.8	30-35

Disadvantages:

1. 30-40% energy loss to produce liquid.
2. Cryogenic container needed.
3. Boiloff losses during dormancy.
4. Safety?
5. Too high tech for general public?

Advantages:

1. Low pressure.
2. Demonstrated on vehicles.
3. Favored by BMW.
4. Can be co-utilized as aircraft fuel.
5. Fair gravimetric capacity.

R&D Needed:

1. More efficient liquifaction (hydride compressors, magnetic & acoustic cooling, etc.)
2. Lower cost, better insulated containers.
3. Automated boiloff capture (e.g., via hydrides) and reliquifaction.

Dehydrogenation/Hydrogenation of Organic Liquids

Example: **Decalin ⇔ Napthaline**

PM-catalyst

<u>Theoretical H-Capacities</u>:
Gravimetric = 7.3 wt.% H_2
Volumetric = 37 kg H_2/m^3

$$C_{10}H_{18} \Leftrightarrow C_{10}H_8 + 5H_2$$

$T_{dehyd} \approx 210^\circ C$

<u>Concept</u>:
1. Onboard catalytic dehydrogenation of organic liquid to provide H_2 gas.
2. Pump dehydrogenated product from vehicle tank for transport to central processing plant (simultaneously refilling tank with fresh H-rich liquid).
3. Rehydrogenate H-depleted liquid back to starting compound and return to filling station.

Hodoshima, Arai, Saito: IJHE, **28** (2003) 197

<u>R&D Needed</u>:
1. Search for organic systems that can be dehydrogenated at low T and produce useable H_2 pressures (i.e., have good thermodynamics).
2. Optimize dehydrogenation catalysts and onboard system.
3. Develop rehydrogenation process and infrastructure scenario.
4. Cost calculations.
5. Safety and toxicity studies.

Liquid Anhydrous Ammonia

Thermal Cracking:

$$NH_3 \rightarrow 0.5N_2 + 1.5H_2$$

T_d = 650-1000˚C

Ni-catalyst

Theoretical H-Capacities:
Gravimetric = 17.7 wt.% H_2
Volumetric = 105 kg H_2/m^3

Concept:
1. Onboard storage of liquid NH_3 at < 25 bar.
2. Onboard catalytic cracking of vaporized NH_3 to provide N_2-H_2 for FC.
3. Direct burning of NH_3 in an IC engine.

Problems:
1. Onboard dissociation system (for FC).
2. Residual NH_3 poisons PEMFC.
3. Toxicity/safety problem.

R&D Needed:
1. Develop high efficiency/low temp cracking catalysts and small, low-cost on-board NH_3 dissociators.
2. Develop thorough H_2 purification system (<10 ppb residual NH_3).
3. Need "fail-safe" onboard tank.
4. Need low-cost, C-free NH_3 production process.
5. Optimize the design of NH_3 ICEs.

G. Thomas, G. Parks: Potential Role of Ammonia in a Hydrogen Economy, DOE, Feb. 2006

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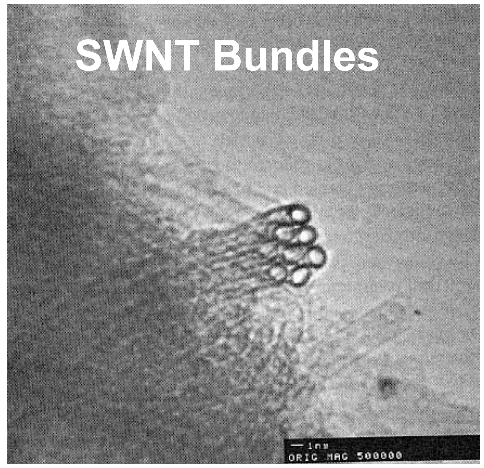
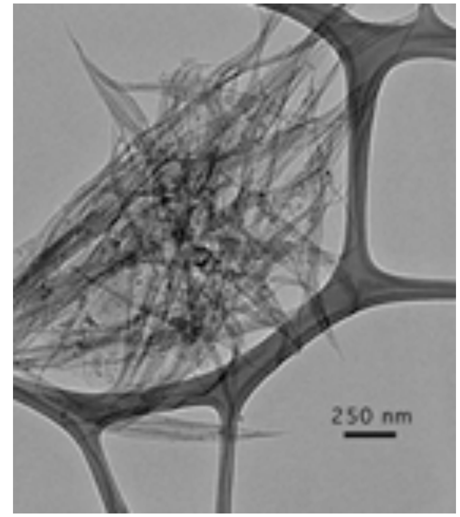
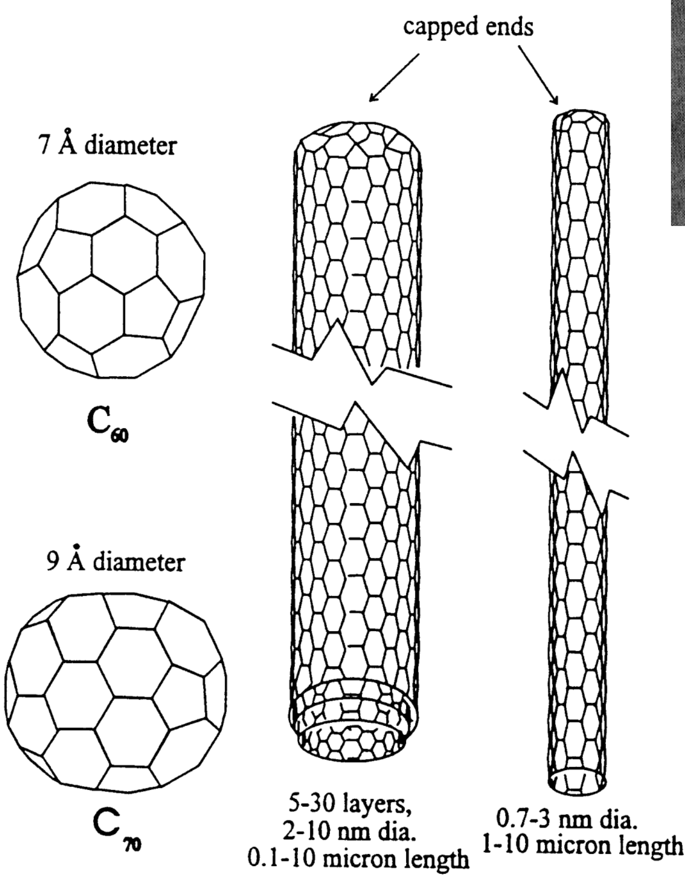
Carbon



Rice Univ, CNST



Heben & Dillon, NREL



Buckyballs **Multi-Wall Nanotubes** **Single-Wall Nanotubes**

<u>Carbon Problems, R&D Directions</u>:

Physisorption: ΔH_{ads} too low, cryogenic

Chemisorption: ΔH_{ads} too high, high T_{des}

Find intermediate bonding strength:

- **Partial substitution (e.g., B, Li, etc.)**
- **Metal insertion (e.g. Pt) for "spillover"**

See presentation by Anne Dillon (NREL)

Zeolites

International Zeolite Association

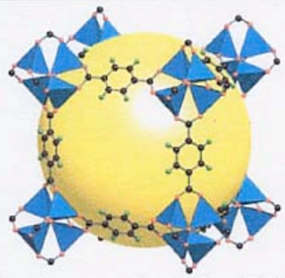
Complex aluminosilicates with specific pore sizes and high surface areas.

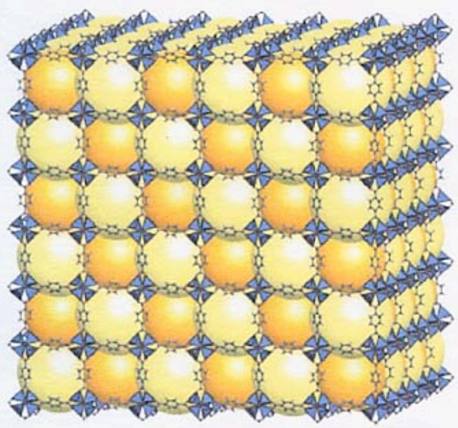
Exist in nature or can be engineered.

Well known as “molecular seives” and catalysts.

Science for capturing non-H_2 gases well known.

Metal-Organic Frameworks (MOFs)


Smallest repeat unit of MOF-5


Extended structure of MOF-5

O.M. Yagi, University of Michigan

Typically ZnO structures bridged by benzene rings.

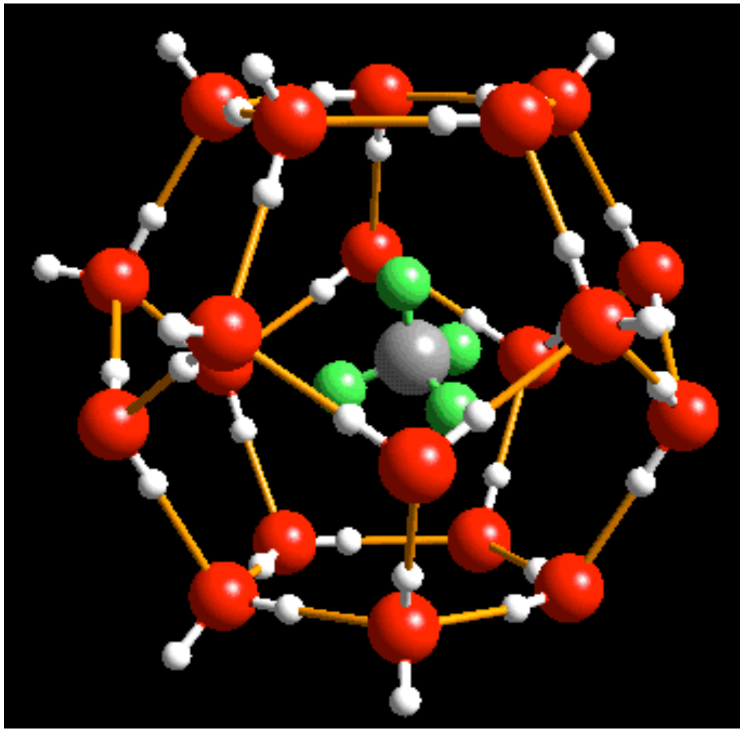
Highly versatile; hundreds of structural variations possible.

Very high surface areas and tunable cage sizes.

Need to increase ΔH_{ads}.

See presentation by Joe Zhao, Texas A&M.

Clathrate Hydrates



W.F. Kuhs, University of Göttingen

H-bonded H_2O cage structures, often containing "guest" molecules like CH_4 and CO_2.

Cage size and structure can often be controlled by organic molecules (e.g., THF).

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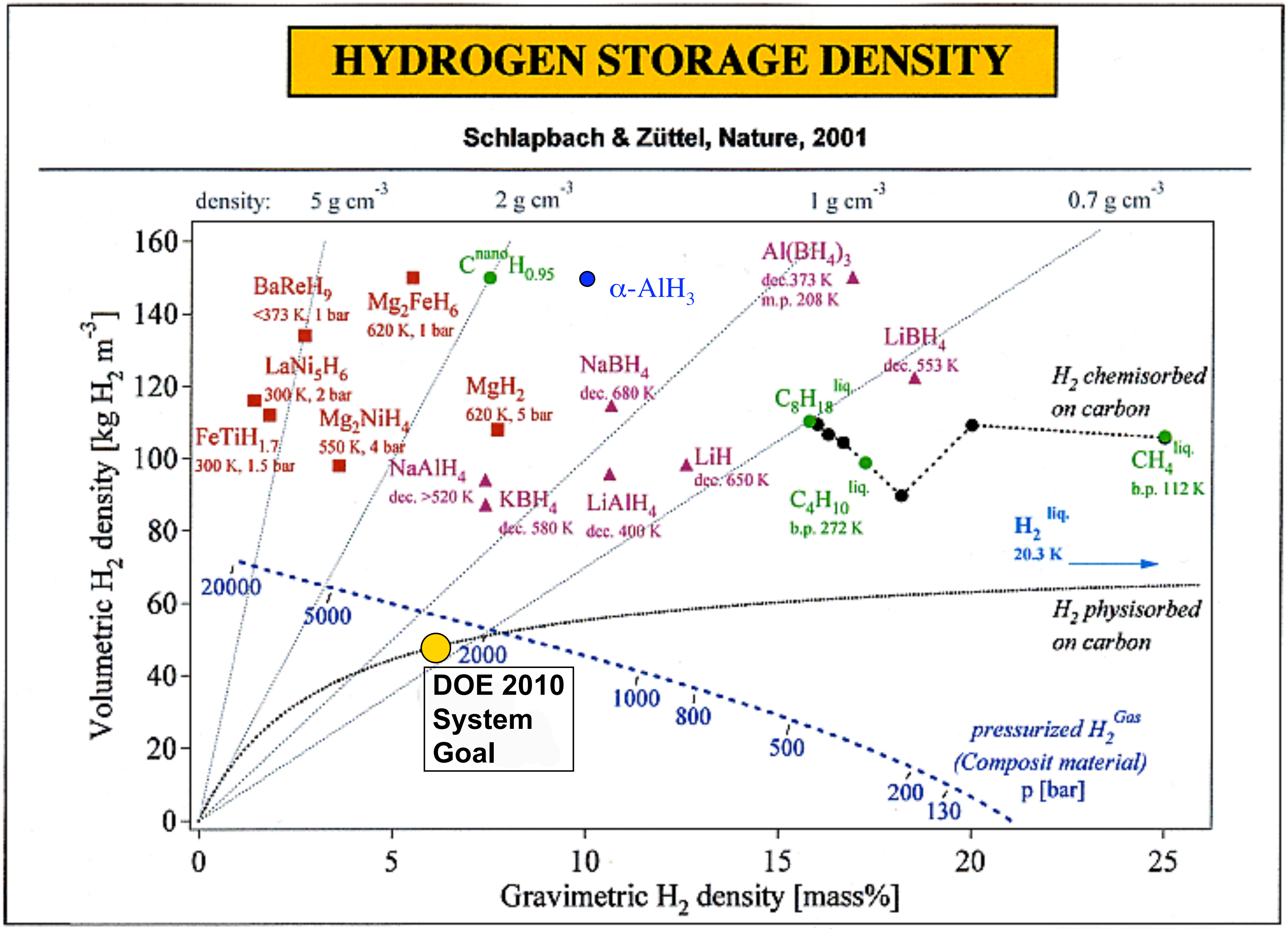


HYDROGEN STORAGE DENSITY
Schlapbach & Züttel, Nature, 2001
density: 5 g cm-3
2 g cm-3
1 g cm-3
0.7 g cm-3
Volumetric H2 density [kg H2 m-3]
Gravimetric H2 density [mass%]
BaReH9
<373 K, 1 bar
Mg2FeH6
620 K, 1 bar
Cnano H0.95
α-AlH3
Al(BH4)3
dec.373 K
m.p. 208 K
LaNi5H6
300 K, 2 bar
MgH2
620 K, 5 bar
NaBH4
dec. 680 K
LiBH4
dec. 553 K
H2 chemisorbed on carbon
FeTiH1.7
300 K, 1.5 bar
Mg2NiH4
550 K, 4 bar
C8H18 liq.
NaAlH4
dec. >520 K
KBH4
dec. 580 K
LiAlH4
dec. 400 K
LiH
dec. 650 K
C4H10 liq.
b.p. 272 K
CH4 liq.
b.p. 112 K
H2 liq.
20.3 K
H2 physisorbed on carbon
20000
5000
2000
1000
800
500
200
130
DOE 2010 System Goal
pressurized H2 Gas
(Composit material)
p [bar]

Chemical Hydride - Ammonia Borane

Decomposition Reaction	wt%H	T, ˚C
$NH_4BH_4 \Rightarrow NH_3BH_3 + H_2$	6.1	<25
$NH_3BH_3 \Rightarrow NH_2BH_2 + H_2$	6.5	<120
$NH_2BH_2 \Rightarrow NHBH + H_2$	6.9	>120
$NHBH \Rightarrow BN + H_2$	7.3	>500

- NH_4BH_4 can be thermally decomposed in 4 steps with very high H_2 yields. Usually start with more stable NH_3BH_3.
- Crystal H-Density ($NH_3BH_3 \rightarrow NHBH$) ≈ 100 g/L
- Nesting in mesoporous "scaffolds" greatly increases decomposition kinetics.
- Catalysis and other approaches to get rapid kinetics <100ºC.
- Gaseous ammonia and boranes can be present in evolved H_2.
- Reactions are not reversible. Offboard regeneration will be required.
- See presentation by Kevin Ott.

Aluminum Hydride, Alane, AlH_3

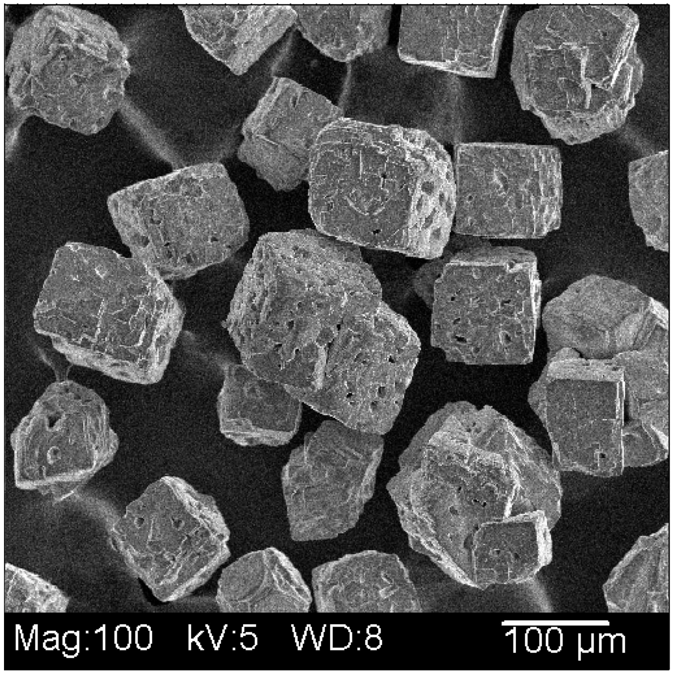
$$\alpha\text{-}AlH_3 \longrightarrow Al + 3/2\ H_2$$

H-capacity (g) = 10.1 wt%

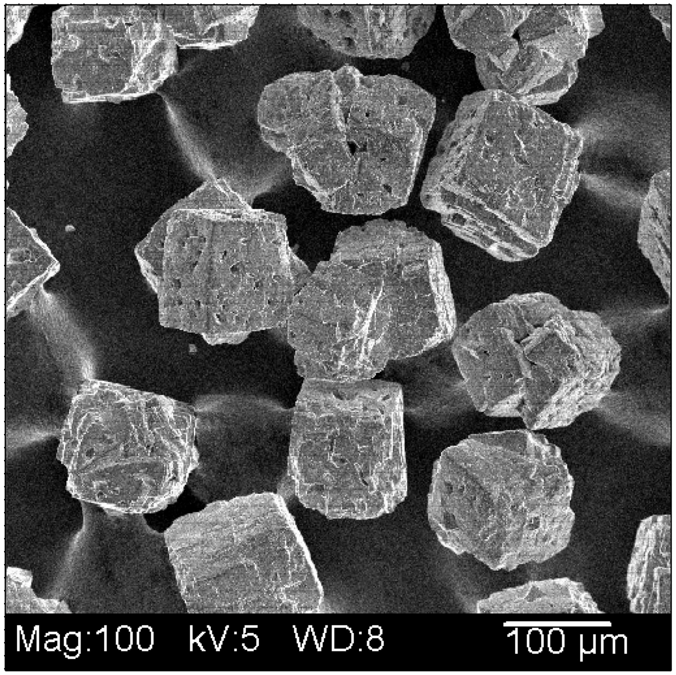
H-capacity (v) = 149 kg/m^3

ΔH_{des} = 7.6 kJ/mol H_2 (only 20% of $NaAlH_4$)

AlH_3



Depleted Al



G. Sandrock et al, Appl. Phys. A, 80 (2005) 687-690.

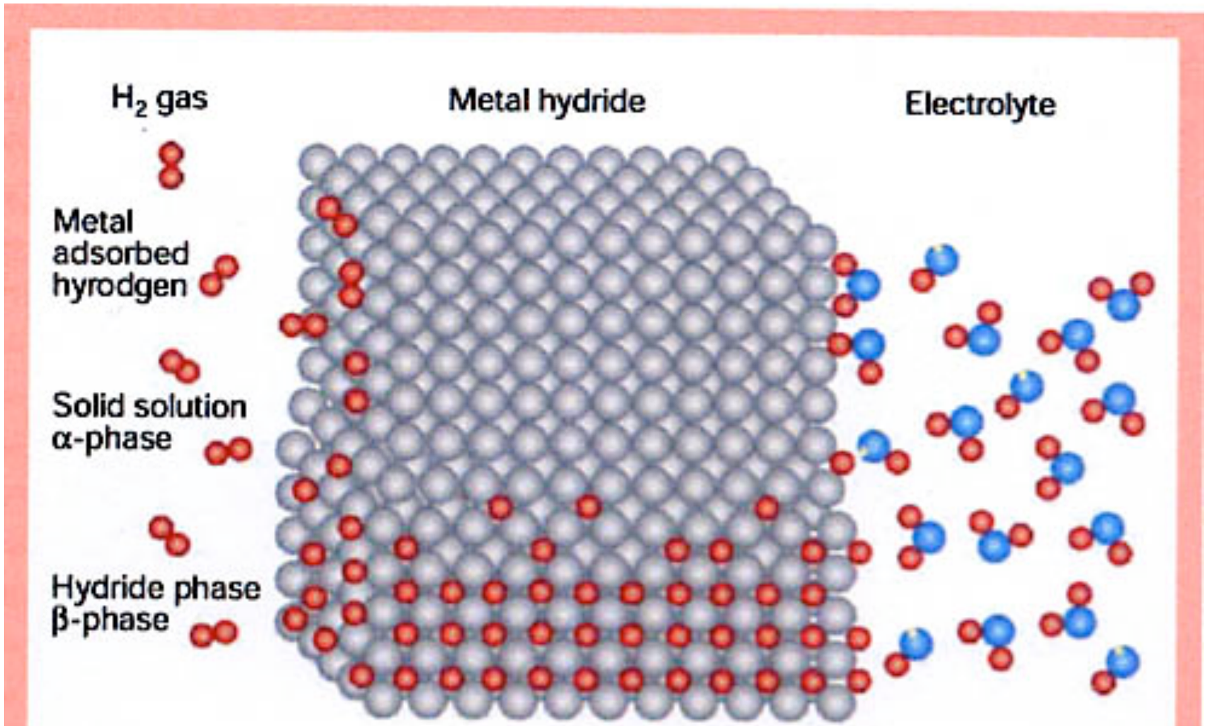
Reversible Hydriding Reactions

Gas Phase:

$$M + \frac{x}{2} H_2 \Leftrightarrow MH_x + heat$$

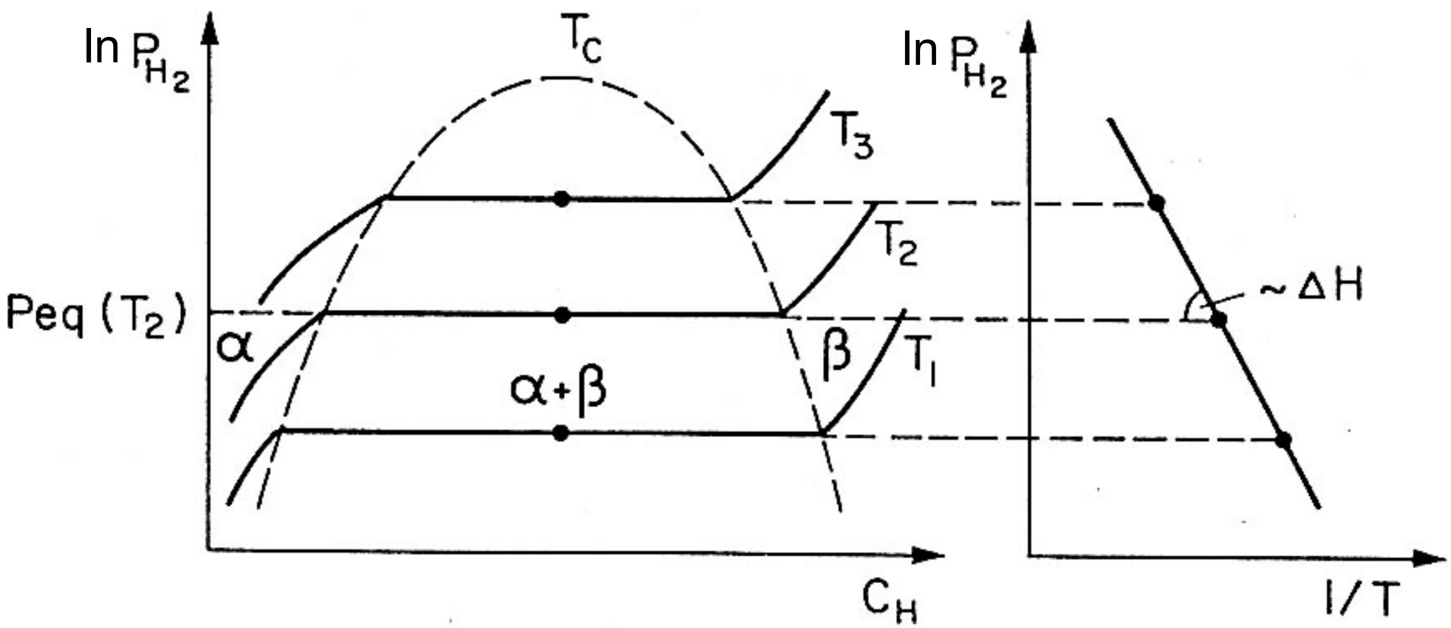
Electrochemical:

$$M + xH_2O + xe^- \Leftrightarrow MH_x + xOH^-$$



Schlapbach, Nature., 2001

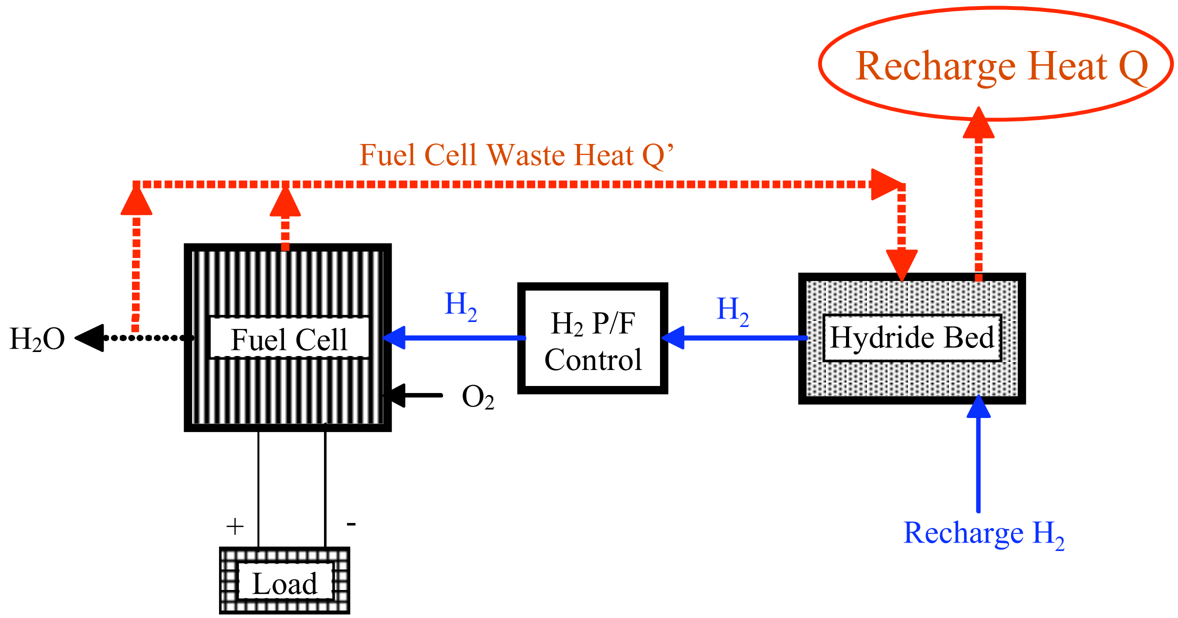
Idealized Pressure-Composition Isotherms
van't Hoff Plot and Equation



$$\ln P_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Schlapbach, Topics in Appl. Phy., 63 (1988)

Onboard Hydride Recharging - The Heat Problem!



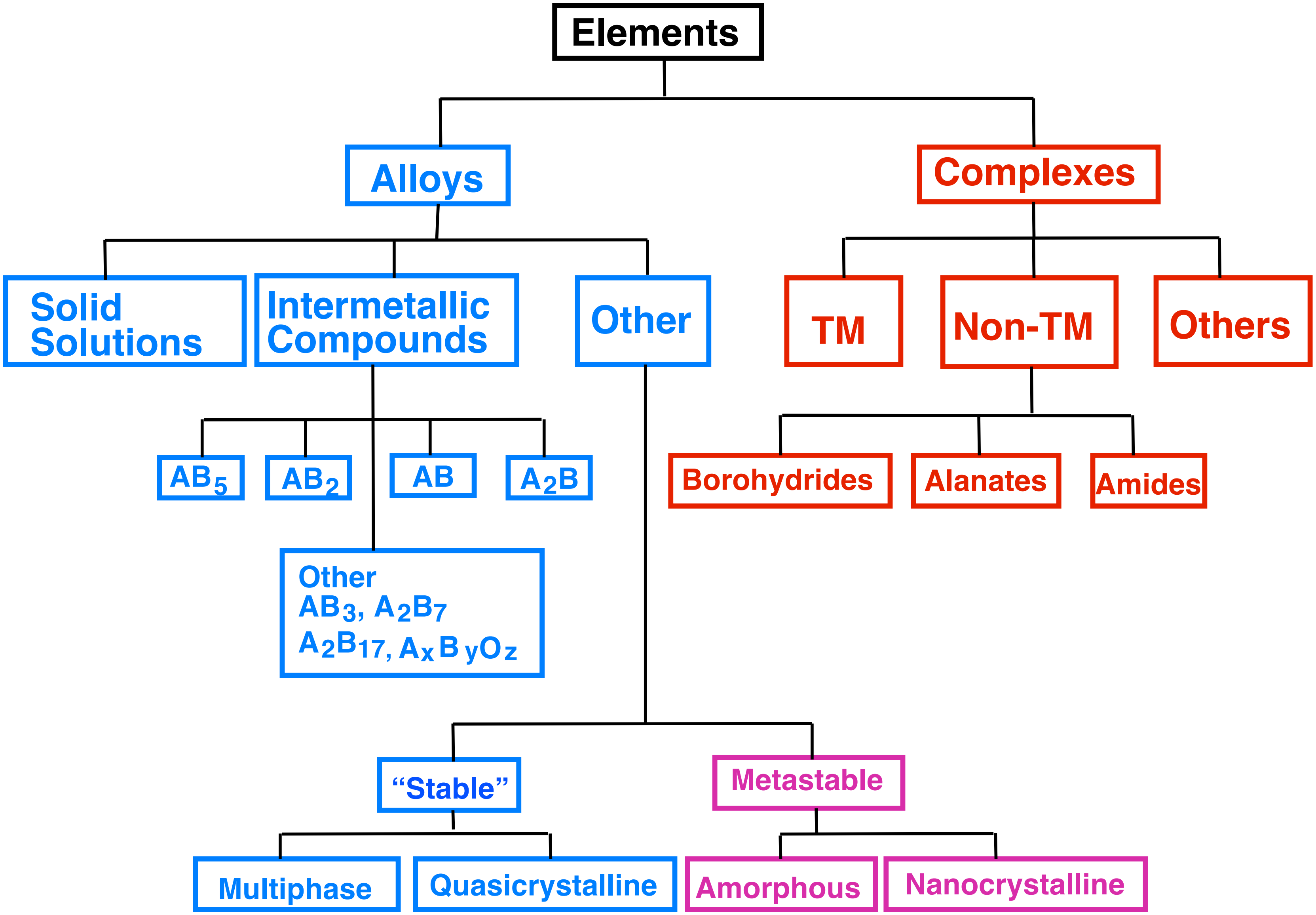
How much heat must be removed during recharging?

DOE 2010 Target = 3 min = 1.67 kg/min (5 kg H_2 tank)

Take as example $NaAlH_4$ (ΔH = -37 kJ/mol H_2)

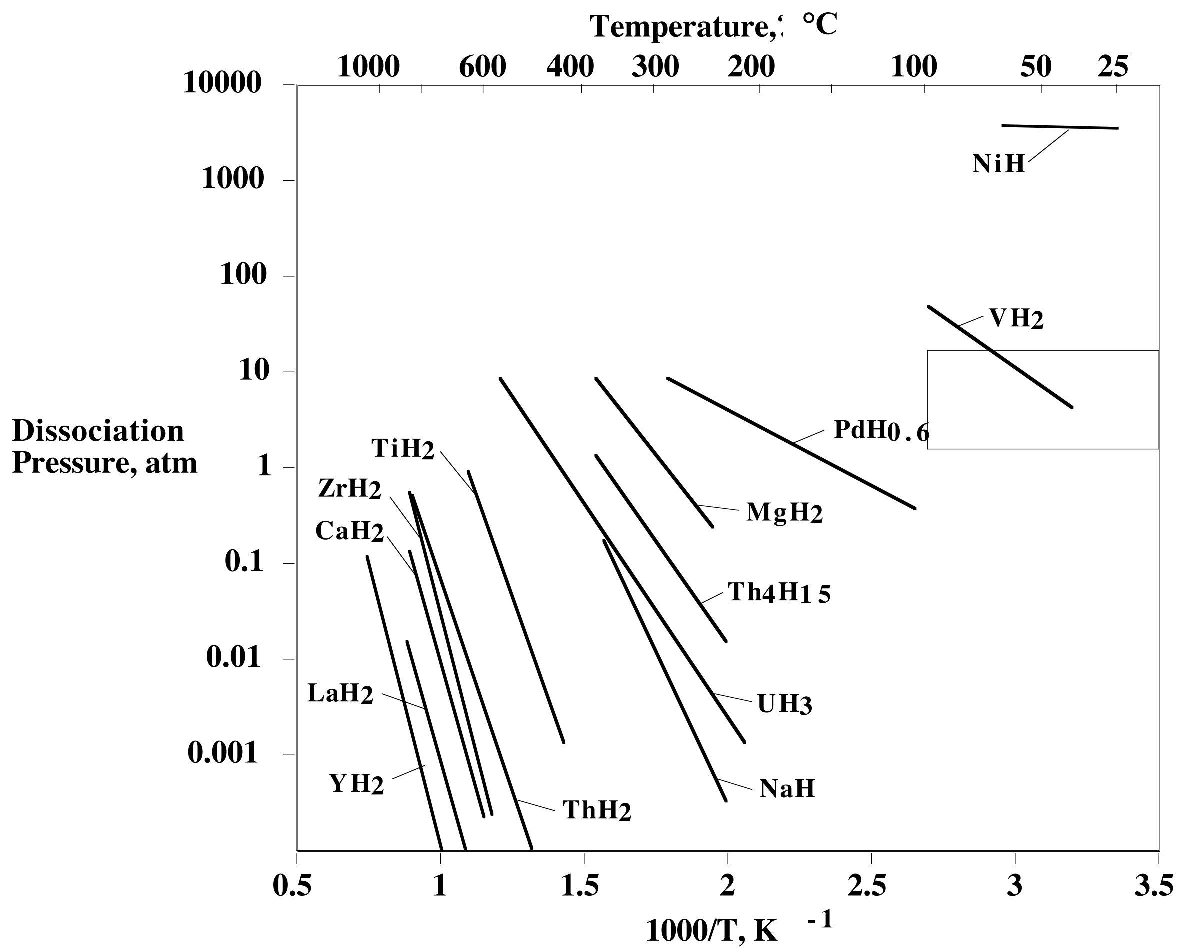
dQ/dt = 510 kW !! $\Rightarrow$ Offboard recharging required?

Metal Hydride Family Tree



Sandrock, after JALCOM, 1999

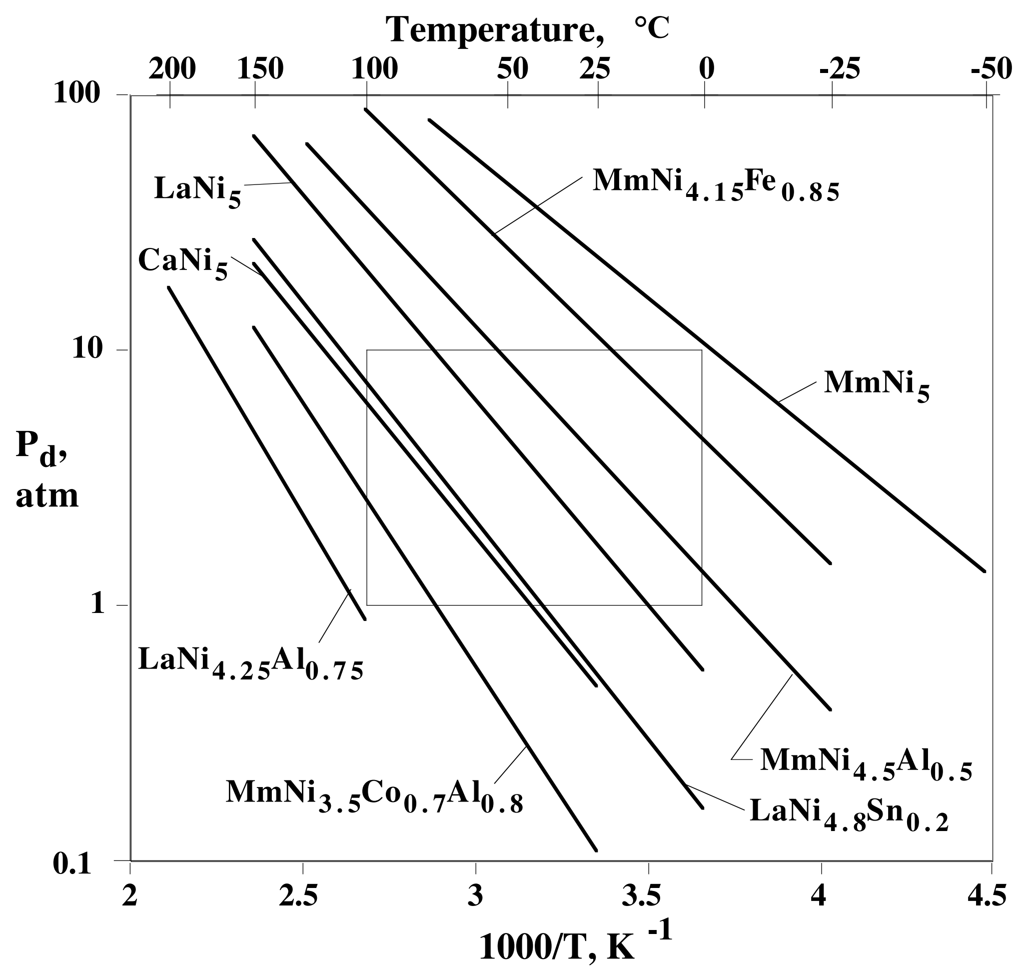
van’t Hoff Lines (Desorption) for Elemental Hydrides



0-100˚C
1-10 ATMA

Sandrock, 1997

van't Hoff Lines (Desorption) for Representative AB_5 Hydrides



Sandrock, 1997

Status and Potential to Meet Targets

(See Metal Hydride Family Tree)

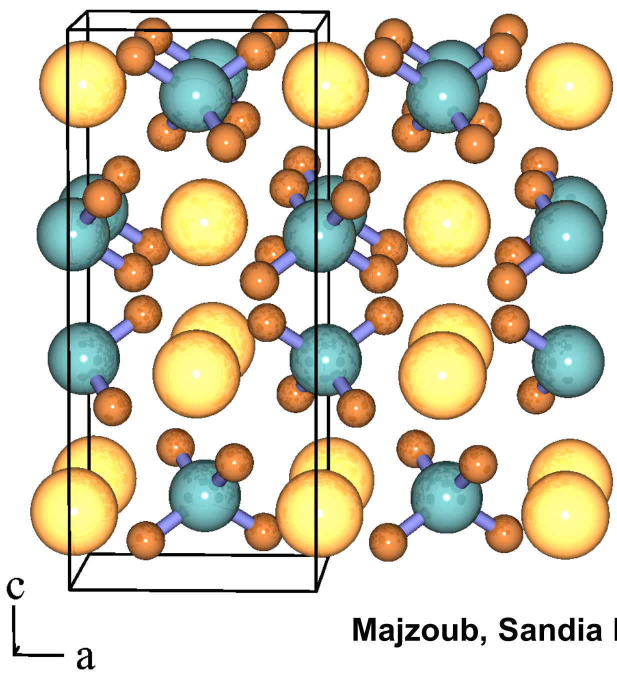
	Elements: Well characterized but thermodynamics unfavorable. Too stable or too unstable to use at T of 0-100˚C. AlH_3 is an interesting possibility.
	Alloys and intermetallic compounds: Very well studied. Many work well at at T<100˚C, but too low gravimetric capacities for vehicles (< 2.5 wt% H). Technically suitable for stationary storage, but rather expensive.
	Nanocrystalline and amorphous: Good kinetics, but H-capacities and 1 bar desorption temperatures not improved.
	Complex: Main hope for the future.

Example of Complex Hydride – Sodium Alanate

$$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \leftrightarrow NaH + Al + 3/2H_2$$

3.7 wt.% H_2 + 1.9 wt.% H_2 = 5.6 wt.% H_2

Needs Ti (or other) "catalyst" for good kinetics and reversibility



Majzoub, Sandia N.L.

Mix of ionic and covalent bonding

$$Na^{+1}\left[\begin{array}{c} H \\ H:Al:H \\ H \end{array}\right]^{-1}$$

Bogdanovic' & Sandrock, MRS Bull., 2002

Borohydrides

Borohydride	wt% H	T_{des}, ˚C
$LiBH_4$	18.5	300
$NaBH_4$	10.6	350
KBH_4	7.4	125
$Be(BH_4)_2$	20.8	125
$Al(BH_4)_3$	16.7	200
$Mg(BH_4)_2$	14.9	320
$Ca(BH_4)_2$	11.6	260

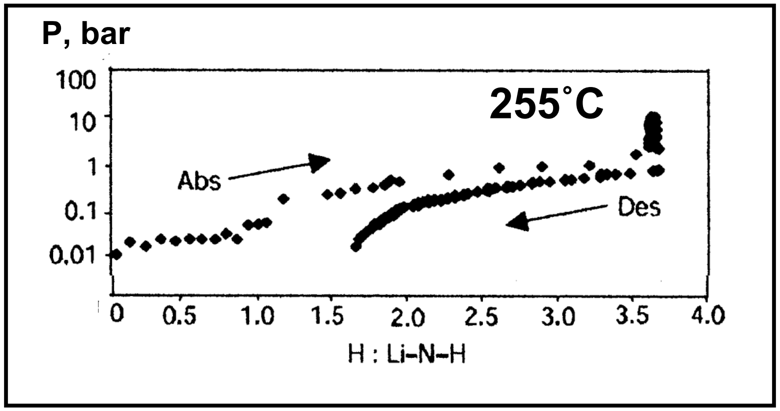
1. Borohydrides have high capacity potential.
2. Not inherently very reversible and often too stable.
3. Can produce diborane with H_2.
4. Benefit from “catalysis”.
5. Significant efforts at enthalpy (ΔH_{des}) “destabilization”.
6. Some progress on $LiBH_4$ and $Mg(BH_4)_2$, reversibility and destabilization.
7. See presentation of Ewa Ronnebro (SNL) and Jean-Philippe Soulie (Iilka).

Hydrogen Storage via Li-Nitrides, Imides and Amides

Chen et al, Nature, **420** (2002) 302

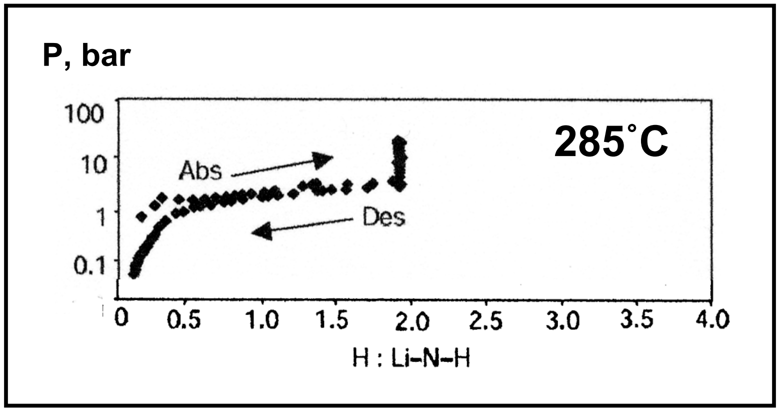
$Li_3N+2H_2 \leftrightarrow Li_2NH+LiH+H_2 \leftrightarrow LiNH_2+2LiH$

(10.4 wt.% H)



$Li_2NH+H_2 \longleftrightarrow LiNH_2+LiH$

6.5 wt.% H @ ΔH = -43 kJ/mol H_2



Extensive work in recent years (e.g., substitution, "catalysis", reaction path chemistry, …)

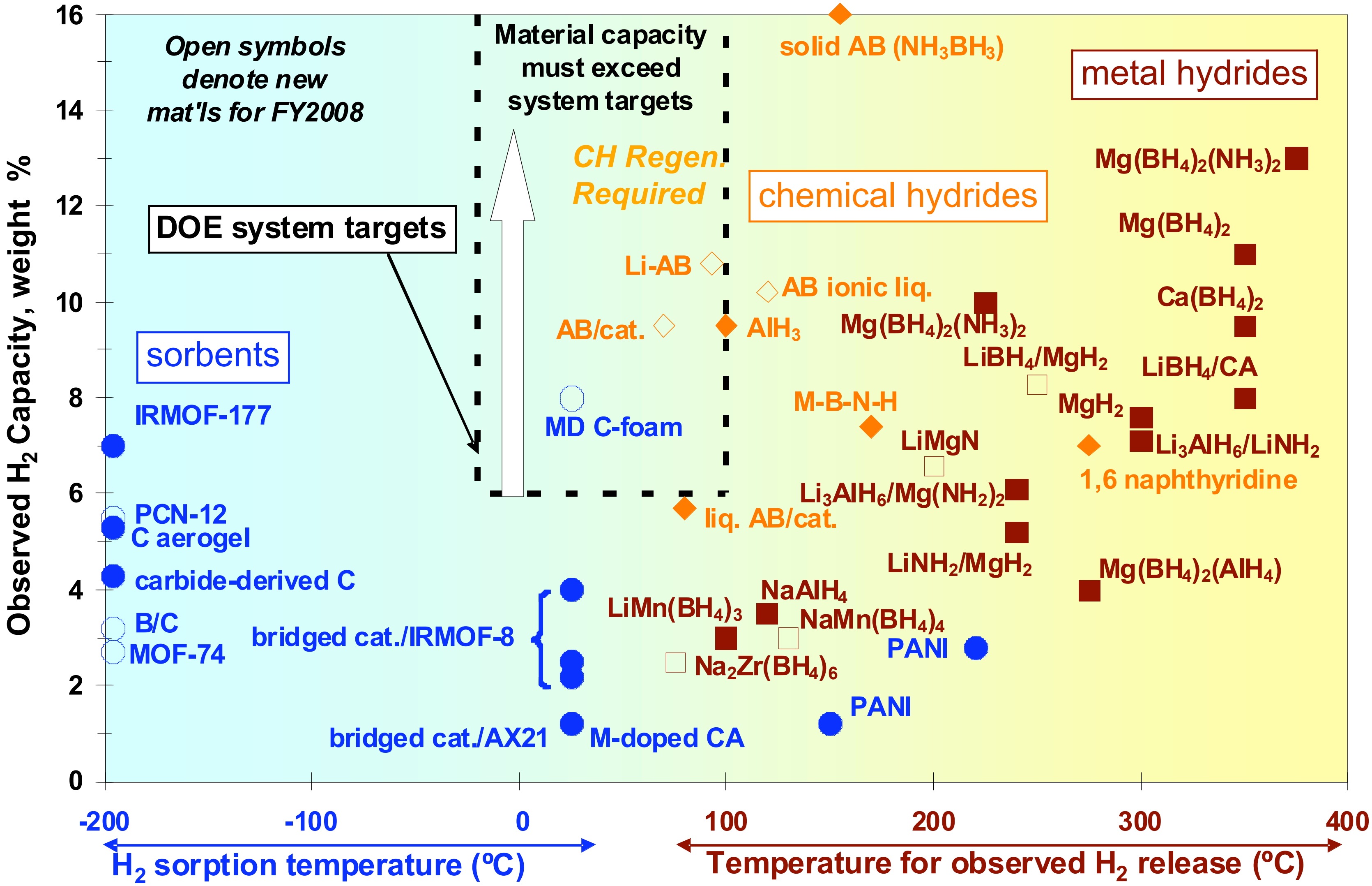
Only the right reaction (6.5 wt% potential) is easily reversible.

Partial Mg substitution lowers ΔH_{des} and T_{des}.

Significant tendency for byproduct NH_3 formation.

Status

Material Capacity vs. Temperature



DOE: G. Thomas (2007), G. Sandrock (2008)

System Status - 2008

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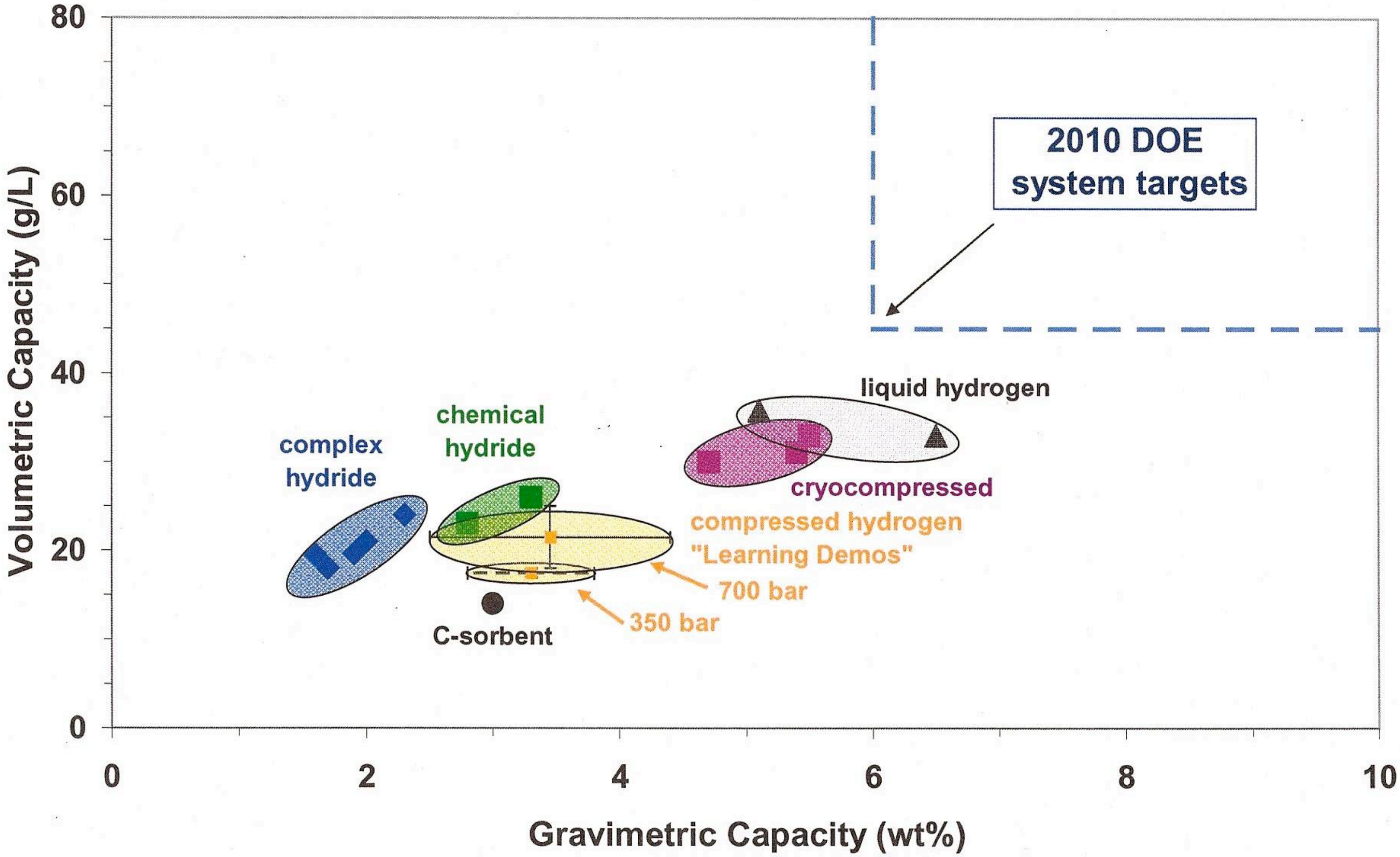

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Possibilities for combinatorial materials science

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